

Electronegativity in quantum electronic transport

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Electronegativity is shown to control charge transfer, energy level alignments, and electron currents in single molecule tunnel junctions, all of which are governed by correlations contained within the density matrix. This is demonstrated by the fact that currents calculated from the one-electron reduced density matrix to second order in electron correlation are identical to the currents obtained from the Green's function corrected to second order in electron self-energy.

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Prediction of electron transport across single molecules requires determination of electronic structure in the presence of open boundary conditions, whether using a non-equilibrium statistical or dynamical theory [1, 2]. Statistical approaches concentrate directly on the non-equilibrium density matrix, whereas if the time evolution for a system driven from equilibrium is followed, attention is usually focused on the non-equilibrium Green's functions (NEGF) describing electron propagation. Treating electronic structure within transport theories requires an understanding of the intriguing and challenging to calculate effects of electron correlations. As exact approaches are limited to model systems or nanostructures with a small number of electrons, attention has focused on improving addition spectra both in the independent electron approximation [3] and by many-body treatments through the GW scheme [4]. In the following, we consider correlation corrections to independent particle models and relate conditions on the one-electron Green's function and reduced density matrix for calculation of currents within non-equilibrium theories. Correlation corrections to the density matrix are shown to correspond to improving ionization potentials (IPs) and electron affinities (EAs) given by Green's functions. This leads to a discussion of electron currents in terms of electronegativity: the impact of the electronegativity on charge transfer, energy level alignments, and current magnitudes is determined.

Electron currents may be calculated from the one-electron reduced density matrix [5, 6] as

$$J(\mathbf{r}) = \frac{1}{2i}[\nabla_{\mathbf{r}} - \nabla_{\mathbf{r}'}]\rho(\mathbf{r}, \mathbf{r}')|_{\mathbf{r}'=\mathbf{r}}, \quad (1)$$

with J the current density, \mathbf{r} a position vector, and ρ the one-electron reduced density matrix (RDM); atomic units are implied unless otherwise given. As the current density operator is a one-body, non-local operator, it is clearly necessary to develop accurate approximations to the RDM to obtain reasonable results. From another viewpoint, calculation of the current can also proceed through computation of the one electron retarded and advanced Green's functions $G_{r,a}$ and application of a Landauer-type formula [7]:

$$I = \frac{1}{\pi} \int d\omega [f_L(\omega; \mu_L) - f_R(\omega; \mu_R)] \text{Tr}[\Gamma_L(\omega) G_a(\omega) \Gamma_R(\omega) \Lambda G_r(\omega)], \quad (2)$$

with electron energy ω , $\Gamma_{L,R}$ spectral densities, $f_{L,R}$ energy distributions with $\mu_{L,R}$ chemical potentials in the left (L) and right (R) electron reservoirs, and Λ is the correction due to correlations weighted by the spectral density of the electrodes and electron-electron spectral density on the molecule. The causal Green's function is related to the RDM via the relation

$$\rho(\mathbf{r}, \mathbf{r}') = \frac{1}{2\pi i} \oint d\omega G(\mathbf{r}, \mathbf{r}'; \omega), \quad (3)$$

with the complex integration performed along the Coulson contour. We begin by pointing out that the reduced density matrix obtained from a many-electron wavefunction corrected to second order in electron correlation is equivalent to the reduced density matrix arising from correcting IPs and EAs in the Green's function to second order in the electron self-energy [8].

To proceed, the energy operator for a molecule within a tunnel junction is written in the form

$$\begin{aligned} \hat{H}(\lambda) = & \int d\mathbf{r} \hat{\psi}^\dagger(\mathbf{r}) h(\mathbf{r}) \hat{\psi}(\mathbf{r}) + \int d\mathbf{r} d\mathbf{r}' \hat{\psi}^\dagger(\mathbf{r}) v_{\text{HF}}(\mathbf{r}, \mathbf{r}') \hat{\psi}(\mathbf{r}') \\ & + \lambda \left[\frac{1}{2} \int d\mathbf{r} d\mathbf{r}' \hat{\psi}^\dagger(\mathbf{r}) \hat{\psi}^\dagger(\mathbf{r}') v(\mathbf{r}, \mathbf{r}') \hat{\psi}(\mathbf{r}') \hat{\psi}(\mathbf{r}) - \int d\mathbf{r} d\mathbf{r}' \hat{\psi}^\dagger(\mathbf{r}) v_{\text{HF}}(\mathbf{r}, \mathbf{r}') \hat{\psi}(\mathbf{r}') \right], \end{aligned} \quad (4)$$

with v the electron-electron interaction on the molecular region, v_{HF} the Hartree-Fock potential and $\hat{\psi}^\dagger, \hat{\psi}$ are second quantized electron field operators. It is assumed that the Fock equations have been solved with electrode self-energies $\Sigma^{L,R}$ to describe the interaction between the molecular region electrons and electrons in the reservoirs; external potentials are also included in the Fock operator. For $\lambda = 0$, the Hamiltonian reduces to the Fock operator

$$\hat{H}(0) = \hat{F} = \sum_p \epsilon_p \hat{a}_p^\dagger \hat{a}_p \quad (5)$$

with \hat{a}^\dagger, \hat{a} creation and annihilation operators for Hartree-Fock states. For $\lambda = 1$, the many-electron Hamiltonian is restored. A perturbation expansion in λ is written for the many-electron wavefunction:

$$|\Psi\rangle = |\Psi^{(0)}\rangle + \lambda |\Psi^{(1)}\rangle + \lambda^2 |\Psi^{(2)}\rangle + \dots \quad (6)$$

For our choice of 0^{th} order approximation, Brillouin's theorem insures that the first order wavefunction consists of only double electron excitations, on the other hand the second order term includes single through quadruple excitations. From

$$\rho(\mathbf{r}, \mathbf{r}') = \langle \Psi | \hat{\psi}^\dagger(\mathbf{r}') \hat{\psi}(\mathbf{r}) | \Psi \rangle, \quad (7)$$

to first order in λ the correction to the 0^{th} order density matrix vanishes [9]. The density matrix to second order is

$$\rho \approx \rho^{(0)} + \lambda^2 \rho^{(2)}. \quad (8)$$

The RDM may be represented as an infinite expansion over single electron states ϕ

$$\rho(\mathbf{r}, \mathbf{r}') = \sum_{pq} \rho_{pq} \phi_q^*(\mathbf{r}') \phi_p(\mathbf{r}). \quad (9)$$

Explicit calculation of the density matrix coefficients from eq. 6 through second order in λ yields

$$\rho_{ij} = \delta_{ij} - \frac{1}{2} \sum_{abk} \frac{\langle ab||ik \rangle \langle jk||ab \rangle}{(\epsilon_i + \epsilon_k - \epsilon_a - \epsilon_b)(\epsilon_j + \epsilon_k - \epsilon_a - \epsilon_b)} \quad (10)$$

$$\rho_{ab} = \frac{1}{2} \sum_{ijc} \frac{\langle ij||ac \rangle \langle bc||ij \rangle}{(\epsilon_i + \epsilon_j - \epsilon_c - \epsilon_a)(\epsilon_i + \epsilon_j - \epsilon_c - \epsilon_b)} \quad (11)$$

$$\rho_{ia} = \frac{1}{2} \sum_{abj} \frac{\langle ab||ij \rangle \langle aj||ab \rangle}{(\epsilon_i - \epsilon_a)(\epsilon_i + \epsilon_j - \epsilon_a - \epsilon_b)} - \frac{1}{2} \sum_{ijb} \frac{\langle ij||ib \rangle \langle ab||ij \rangle}{(\epsilon_i - \epsilon_a)(\epsilon_i + \epsilon_j - \epsilon_a - \epsilon_b)} \quad (12)$$

with $\langle pq||rs \rangle = \langle pq|v|rs \rangle - \langle pq|v|sr \rangle$. We use the convention whereby indices i, j, k, \dots label occupied, a, b, c, \dots label unoccupied, and p, q, r, \dots are used to label general (occupied or unoccupied) states in $|\Psi^{(0)}\rangle$.

Transmission resonances are given through the poles of the Green's functions and can be identified as IPs and EAs. Hence, it is reasonable to assume that if an independent particle picture is chosen to optimize IPs and EAs, it follows that prediction of currents from the NEGF approach will be improved. In this context, a model for transport is measured in terms of reproducing the molecular electronegativity. It is known that introduction of correlation corrections beyond independent particle models for the Green's function improves the prediction of IPs and EAs. The Green's function with second order self-energies has been studied by Pickup and Goscinski [8] leading to the following approximation

$$\begin{aligned} [G^{(2)}(\omega)]_{pq}^{-1} &= [G^{(0)}(\omega)]_{pq}^{-1} + \Sigma^{(2)}(\omega)_{pq} \\ &= (\omega - \epsilon_p)\delta_{pq} - \frac{1}{2} \sum_{iab} \frac{\langle ab||pi \rangle \langle qi||ab \rangle}{\omega + \epsilon_i - \epsilon_a - \epsilon_b} - \frac{1}{2} \sum_{ija} \frac{\langle ij||pa \rangle \langle qa||ij \rangle}{\omega + \epsilon_a - \epsilon_i - \epsilon_j}. \end{aligned} \quad (13)$$

The lowest order improvement to Koopmans' IPs and EAs are obtained from the poles of the diagonal elements of $G(\omega)$. It is found the self-energy corrects Koopmans' IP ϵ_i through terms describing orbital relaxation and pair correlations; a similar interpretation holds for corrections to the EAs [8]. Within this approximation, it is also possible to determine the density matrix directly from eq. 3; the resulting density matrix coincides *exactly* with the density matrix calculated from eq. 6 through $O(\lambda^2)$. Hence calculating the density matrix through second order in electron correlation and correcting IPs and EAs with second order self-energies $\Sigma^{(2)}$ will lead to the same predictions for electron current. For moderate electron correlations, improving spectra for independent particle models or explicitly including correlations in the RDM are equivalent.

Recently a criterion for selecting an independent particle model for quantum electronic transport was given as the set of single particle states yielding an approximate density matrix with maximal overlap to the exact RDM [10]. The single electron states diagonalizing the RDM are natural orbitals (NOs) [11] and their eigenvalues ρ_i are known as

natural occupations. If one asks what is the best finite expansion approximation $\tilde{\rho}$ to the exact RDM

$$\Delta\rho = \int |\rho - \tilde{\rho}|^2 d\mathbf{r} d\mathbf{r}', \quad (14)$$

it is found that including the first n natural orbitals with the largest occupancies for a truncated expansion eq. 9 fulfills the least squares condition [9]. We consider the couplings between density matrix coefficients in eq. 10 by writing

$$\rho = \begin{bmatrix} \rho_{ij} & \rho_{ia} \\ \rho_{ai} & \rho_{ab} \end{bmatrix}, \quad (15)$$

with (ij) , (ab) , and (ia) denoting occupied-occupied, unoccupied-unoccupied, and occupied-unoccupied spaces respectively, with occupations referred to the 0^{th} order wavefunction. The natural orbitals to second order in electron correlation are given by the eigenfunctions of eq. 15. Constructing the “best” independent particle picture in the sense of eq. 14 implies occupying a single Slater determinant by the first n_e natural orbitals. We have previously shown numerically that a single determinant composed of the largest occupation number NOs can lead to essentially the same results as a full many-body treatment for tunneling through alkanes [10]. For a single determinant approximation, the density matrix is idempotent $\rho^2 = \rho$ which occurs since the first n_e occupations are equal to 1 with all others 0. Hence a measure for the quality of a single determinant approximation is how well the eigenvalues of eq. 15 approximate the idempotency condition. As the ρ_{ia} couplings between the occupied and unoccupied spaces becomes stronger, the occupations of the 0^{th} order states can become significantly less than unity. From many-body theory it is well understood what this condition implies: a single determinant or independent particle picture is no longer useful as a 0^{th} order wavefunction. For weak to moderate correlations, the Green’s function approach can achieve improved IPs and EAs by a low order approximation to the electron self-energy. As natural occupancies in the 0^{th} order wavefunction become very much less than unity, a perturbation expansion about an independent particle picture loses meaning and even higher order corrections to $|\Psi^{(0)}\rangle$ will not correct IPs and EAs on the molecular region. In a similar context, this is seen as the failing of the *GW* approximation for systems with multi-determinantal ground states [12] or in strongly correlated electron transport [4]. For strong electron correlations coupled-cluster theory offers a convenient nonperturbative framework from which higher order approximations to the density matrix follow [13], alternatively correlated one particle methods [14] to infinite order can be chosen to yield correct IPs and EAs.

The Mulliken electronegativity given as $(IP + EA)/2$ is a useful measure of charge transfer, and it is charge transfer that determines molecular level alignments relative to electron reservoir energies [15]. Predicting level alignments

correctly for molecules bonded between electrodes is essential for accurate current-voltage characteristics [16]. In the Hartree-Fock approximation, charge transfer is under-estimated as hybridization to virtual states is weak. In the local density (LDA) and generalized gradient (GGA) approximations to density functional theory (DFT), charge transfer is over-estimated [17]. These effects are demonstrated for the case of hexanedithiol bonded between two gold clusters in fig. 1 where the highest occupied-lowest unoccupied energy gap in the molecular orbitals (HOMO-LUMO gap) and molecular electronegativity is given against charge transfer relative to molecular hexanedithiol. For a large HOMO-LUMO gap or weak electronegativity, charge transfer is small. For small HOMO-LUMO gaps typical of GGA and LDA, over-estimation of charge transfer is confirmed. Hybrid functionals correct the charge transfer to some extent, but this correction is not systematic [17].

We introduce a simple correlated model for a molecular chain and investigate the effect of over- and under-estimation of electronegativity on electron transport. We use the following model Hamiltonian for an infinite chain:

$$\begin{aligned}
\hat{H} = & - \gamma_L \sum_{n < -3} (\hat{c}_n^\dagger \hat{c}_{n-1} + h.c.) + \sum_{n < -3} (\epsilon_L + V_L) \hat{c}_n^\dagger \hat{c}_n - \gamma_{LM} (\hat{c}_{-4}^\dagger \hat{b}_{-3} + h.c.) \\
& + \sum_{n=-3}^{+3} (\epsilon_M + V_n) \hat{b}_n^\dagger \hat{b}_n - \gamma_M (\hat{b}_{-3}^\dagger \hat{b}_{-2} + \hat{b}_{-1}^\dagger \hat{b}_1 + \hat{b}_2^\dagger \hat{b}_3 + h.c.) - \Gamma_M (\hat{b}_{-2}^\dagger \hat{b}_{-1} + \hat{b}_1^\dagger \hat{b}_2 + h.c.) \\
& - \gamma_{MR} (\hat{b}_{+3}^\dagger \hat{c}_{+4} + h.c.) + \sum_{n > +3} (\epsilon_R + V_R) \hat{c}_n^\dagger \hat{c}_n - \gamma_R \sum_{n > +3} (\hat{c}_n^\dagger \hat{c}_{n+1} + h.c.)
\end{aligned} \tag{16}$$

Six central sites of the chain are labelled -3, -2, -1, 1, 2, 3 (i.e. there is no 0 site) and are treated as the molecular region with \hat{b}^\dagger, \hat{b} creation and annihilation operators for electrons on the molecule. The electron reservoirs are described by the atomic sites extending towards the left and right away from the central molecular sites with creation and annihilation operators \hat{c}^\dagger, \hat{c} for the reservoir electrons. The site energies are given by $\epsilon_L = \epsilon_R$ and ϵ_M for the reservoir and molecular regions, respectively. The volage applied across the molecular junction is described by the voltages $V_L \neq V_R$ in the reservoirs and the voltage drop V_n across the molecular sites is scaled linearly between the values V_L and V_R . The nearest neighbor interactions are $\gamma_L = \gamma_R$ within the electrode regions, and there are two molecular site-site interaction Γ_M and γ_M representing single and double bonds, respectively, on the molecular region as a simple model for hexanedithiol, and $\gamma_{LM} = \gamma_{MR}$ determine the molecule-electrode couplings. The eigenstates of the molecular Hamiltonian are found with the electron-electron self-energies and exact electrode self-energies are introduced describing coupling to the electrodes [18]. The resulting single electron states are taken as the expansion functions for the correlated version of the model obtained from $\hat{H}_0 \rightarrow \hat{H}_0 + \hat{v}$, with \hat{v} the pairwise perturbation interactions about the mean field solution as in eq. 4 with $\lambda = 1$. Current-voltage characteristics are calculated using

eq. 2. We use a simplified form of the self-energy such that the interaction matrix elements in eq. 13 are approximated as $\langle pq||rs \rangle \approx U$. In fig. 2, the HOMO-LUMO gap for the molecular region is given as a function of U demonstrating that the electronegativity on the molecular region may be systematically controlled through the electron-electron self-energies. The results for the current voltage characteristics from the model are presented in fig. 3. The independent particle or uncorrelated model occurs for $U = 0$ and increasing U corresponds to increasing electron correlations on the molecular region. At $U = 0$, currents at low voltages are much lower than when the $\Sigma^{(2)}$ term is allowed to correct IPs and EAs; in this case, the highest lying occupied states are too low (IPs too high) and the lowest lying unoccupied single electron states are too high (EAs too low) with respect to the Fermi level. Under these conditions neither occupied or unoccupied states enter into the voltage bias window at low voltages, and this level of electronic structure treatment corresponds to a Hartree-Fock approximation. Increasing correlations on the molecular region, the highest occupied states near the Fermi level enter the bias window at lower values of voltage, followed by the introduction of the unoccupied states at higher voltage bias (this sequence is due to the relative position of the Fermi level relative to occupied and unoccupied states for this example). The correlations on the molecular region serve to shift up occupied levels relative to the Fermi level leading to reduced IPs, whereas increasing correlations systematically lower the lowest lying unoccupied states leading to increased EAs. Increasing correlations continue to reduce the IPs and increase EAs until eventually electronegativity is under-estimated. The impact on the current-voltage characteristics is that the molecular levels enter the bias window at very low values of applied voltage resulting in large current magnitudes. Larger values of U correspond to the use of LDA or GGA exchange-correlation potentials within DFT where the strong over-estimation of charge transfer is known to occur [17]. Hartree-Fock and Kohn-Sham (using LDA or GGA) orbitals are not appropriate independent particle models for electron transport due to strong under- and over-estimation of charge transfer, respectively. The results of fig. 3 clearly show the impact on current voltage characteristics for these two extremes.

Correcting electronegativity is equivalent to maximizing overlap to the reduced density matrix: this is true to low orders in electron correlation and of course the correct electronegativity and density matrix are found at the exact many-body solution. In general, improving descriptions for the RDM and electronegativity with the methods described will lead to improved prediction of electron currents in systems with moderate electron correlations. The best independent particle picture within this context is a single determinant comprised of natural orbitals; any attempt to refine single electron models for transport should lead to electron wavefunctions that approximate natural orbitals.

In the case of Green’s function approaches, moderate electron correlations imply the need to include electron-electron self-energies to describe quasi-particle propagation. For strong correlations, a single determinant wave function is not an adequate approximation to predict IPs and EAs and perturbation corrections about a single reference state fail- thus complicating treatment of molecular junctions with Green’s function approaches. However, in all cases, from weak to strong correlations, the criterion to maximize overlap to the exact reduced density matrix leads to improved predictions for electron currents.

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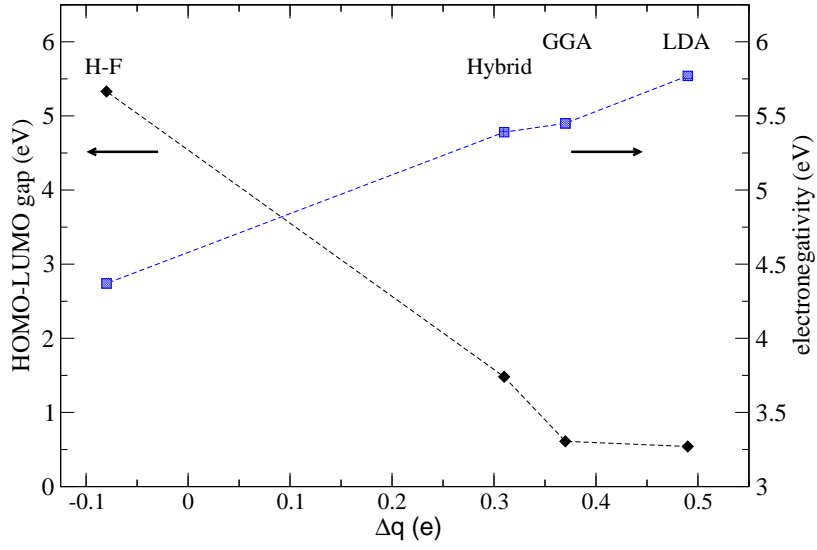


FIG. 1: Highest occupied and lowest unoccupied (HOMO-LUMO) energy gap and electronegativity versus charge transfer for hexanedithiol bonded to linear gold chains. Calculations have been performed with the TURBOMOLE program system [19]. All calculations have been performed using the auc-cc-pVDZ basis set for carbon [20] and split valence polarized valence basis for all other atoms, including a sixty electron effective core potential for the gold atoms [19]. Calculations have been performed using the Hartree-Fock and density functional theory calculations using hybrid (B3-LYP), generalized gradient approximation (GGA/PBE), and local density approximation (LDA/PW) exchange-correlation functionals.

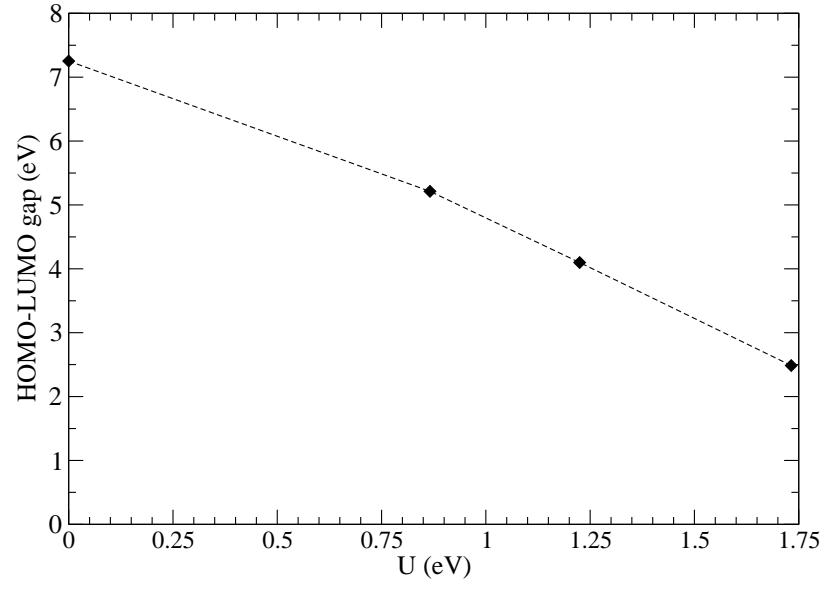


FIG. 2: HOMO-LUMO gap for the model system defined by eq. 16 as a function of the electron-electron self energy as varied through the interaction parameter U . The reduction in the gap demonstrates the effect of electron-electron self-energy on the molecular electronegativity.

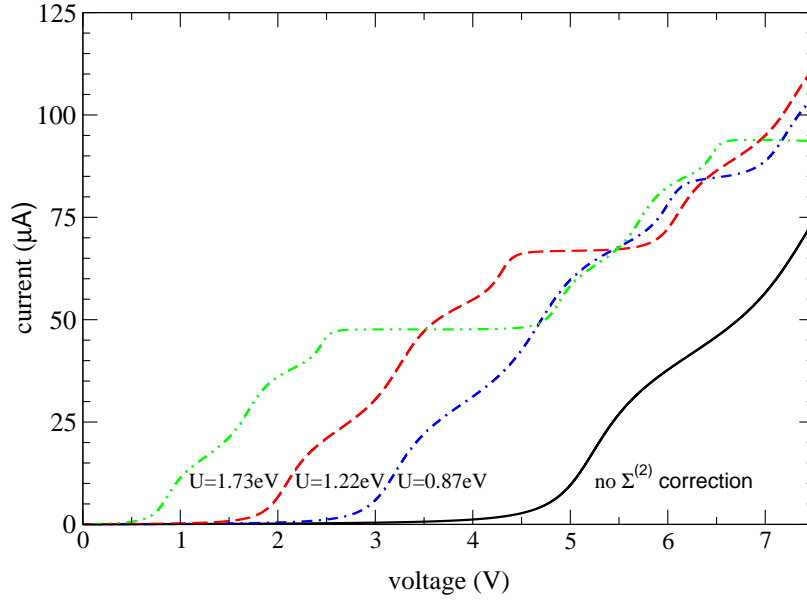


FIG. 3: Current voltage characteristics for the model Hamiltonian of eq. 16. $\epsilon_M = 1.0\text{eV}$, $\epsilon_L = \epsilon_R = \epsilon_{\text{Fermi}} = 0.0$, $\gamma_M = 4.54\text{eV}$, $\Gamma_M = 1.5\text{eV}$, $\gamma_L = \gamma_R = 10.0\text{eV}$, $\gamma_{LM} = \gamma_{MR} = 2.4\text{eV}$. Electronegativity is modified by varying U , with values as labeled within the figure.